



ACQUISITION AND  
TECHNOLOGY

OFFICE OF THE UNDER SECRETARY OF DEFENSE

3000 DEFENSE PENTAGON  
WASHINGTON DC 20301-3000

June 10, 2002



MEMORANDUM FOR U.S. MISSION TO NATO, ARMAMENTS COOPERATION DIVISION  
(ARMY ARMAMENTS OFFICER), PSC 81, APO AE 09724

SUBJECT: Draft STANAG 4515 (EDITION 1) – “EXPLOSIVES: THERMAL  
CHARACTERIZATION BY DIFFERENTIAL THERMAL ANALYSES, DIFFERENTIAL  
SCANNING CALORIMETRY ”

Reference document, AC/310-D/190, 21 September 2001, SAB.

The U.S. Armed Forces ratifies the referenced agreement.

Ratification and implementation details are as follows:

IMPLEMENTATION

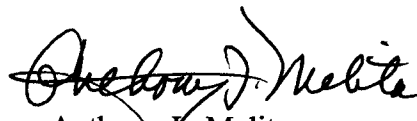
	Forecast Date	Actual Date
<u>RATIFICATION REFERENCE</u>	<u>NAVY ARMY AIR FORCE</u>	<u>NAVY ARMY AIR FORCE</u>
Memo, OUSD(A&T) DATED AS ABOVE	June 10, 2002	June 10, 2002

NATIONAL IMPLEMENTING DOCUMENT: None, the STANAG is self-implementing.

RESERVATIONS: None

COMMENTS: None

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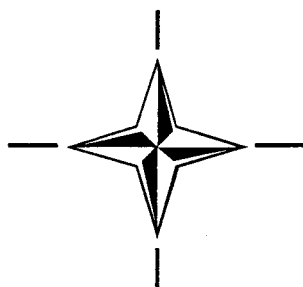
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STANAG 4515  
(Edition 1)

**NORTH ATLANTIC TREATY ORGANIZATION  
(NATO)**



**NATO STANDARDIZATION AGENCY  
(NSA)**

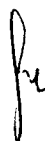
**STANDARDIZATION AGREEMENT  
(STANAG)**

SUBJECT: EXPLOSIVES: THERMAL CHARACTERIZATION BY DIFFERENTIAL  
THERMAL ANALYSIS, DIFFERENTIAL SCANNING CALORIMETRY  
AND THERMOGRAVIMETRIC ANALYSIS

Promulgated on 23 August 2002



Jan H ERIKSEN  
Rear Admiral, NONA  
Director, NSA



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STANAG 4515  
(Edition 1)

RECORD OF AMENDMENTS

No.	Reference/date of amendment	Date entered	Signature

EXPLANATORY NOTES

AGREEMENT

1. This NATO Standardization Agreement (STANAG) is promulgated by the Director, NSA under the authority vested in him by the NATO Military Committee.
2. No departure may be made from the agreement without consultation with the tasking authority. Nations may propose changes at any time to the tasking authority where they will be processed in the same manner as the original agreement.
3. Ratifying nations have agreed that national orders, manuals and instructions implementing this STANAG will include a reference to the STANAG number for purposes of identification.

DEFINITIONS

4. Ratification is "In NATO Standardization, the fulfilment by which a member nation formally accepts, with or without reservation, the content of a Standardization Agreement" (AAP-6).
5. Implementation is "In NATO Standardization, the fulfilment by a member nation of its obligations as specified in a Standardization Agreement" (AAP-6).
6. Reservation is "In NATO Standardization, the stated qualification by a member nation that describes the part of a Standardization Agreement that it will not implement or will implement only with limitations" (AAP-6).

RATIFICATION, IMPLEMENTATION AND RESERVATIONS

7. Page (iii) gives the details of ratification and implementation of this agreement. If no details are shown it signifies that the nation has not yet notified the tasking authority of its intentions. Page (iv) (and subsequent) gives details of reservations and proprietary rights that have been stated.

FEEDBACK

8. Any comments concerning this publication should be directed to NATO/NSA - Bvd Leopold III, 1110 Brussels - BE.

NATO/PfP SANS CLASSIFICATION

STANAG 4515  
(Edition 1)

NAVY/ARMY/AIR

NATO STANDARDIZATION AGREEMENT  
(STANAG)

EXPLOSIVES: THERMAL CHARACTERIZATION BY DIFFERENTIAL THERMAL ANALYSIS,  
DIFFERENTIAL SCANNING CALORIMETRY AND THERMOGRAVIMETRIC ANALYSIS

Annexes:

- A. Thermal characterization of explosives.
- B. Procedures.
- C. Further investigations possible using the techniques described.
- D. Data sheet for reporting of results.
- E. Figures.
- F. Examples of thermograms.

Related documents:       None

AIM

1. The aim of this agreement is to standardise test procedures for thermal characterization of explosive materials using Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).
2. This agreement is intended for use by the NATO Participating Nations.

AGREEMENT

3. Participating Nations agree to adopt the test procedures described in Annex B for the characterization of explosives using thermal analytical techniques and to use the data sheet at Annex D for reporting test results.

WARNING

4. This STANAG calls for the use of substances and test procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and in no way absolves the user from the statutory obligations relating to health and safety at any stage during use.

IMPLEMENTATION OF THE AGREEMENT

5. This STANAG is considered implemented by a nation when that nation has issued instructions that thermal characterization of explosives shall be performed by the test procedures described in this STANAG.



**THERMAL CHARACTERIZATION OF EXPLOSIVES****1. INTRODUCTION**

- a. Information on the thermal characteristics of explosives is important from a safety and operational viewpoint. Characteristics displayed on thermograms from the major techniques Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) can be used to monitor samples in comparison to controls, to examine if changes have occurred which may affect stability and consequently safety and operation. Differences due to sample preparation, ageing, packing and geometry may be recognised from thermal data.
- b. The major methods used to obtain thermoanalytical data are fairly well established. However, the application of these thermal techniques to the study of explosives requires special considerations due to their mode of operation. Generally, sample size is kept to a minimum for safety reasons since the high rate of energy released on decomposition can lead to "thermal runaway". Instruments are probably unlikely to be able to follow such rapid energy changes and data can be lost or wrongly interpreted as a result. Heating rates are, therefore, carefully chosen to match sample size in order to keep the reactions under control while producing signals with measurable magnitude.
- c. The primary techniques used to obtain information on thermal properties are DTA, DSC and TGA. Each technique is valuable by itself but additional information may be gained using combined techniques such as DTA/TGA and TGA linked to a Fourier Transform Infrared Spectrometer for evolved gas analysis (EGA) or to a mass spectrometer (MS). DTA studies tend to yield similar information to that generated by DSC. DTA instrumentation, however, is generally more robust and consequently larger samples and higher heating rates can often be used quite safely. The technique is particularly useful for the study of ignition temperatures of pyrotechnics and primary explosives when a photodetector system is used to monitor the "flash" associated with ignition. DSC is more suitable than DTA for accurate quantitative analysis, the data generated from a DTA instrument should only be considered as semi-quantitative.
- d. Dynamically gained data cannot normally be used directly for determining the isothermal storage conditions of explosives. For example, the dynamic decomposition temperature depends strongly on experimental conditions. In any case this temperature is much higher than the tolerable temperature of isothermal storage.

**2. GENERALISED THERMAL ANALYSIS SYSTEM**

- a. All thermal analysis techniques operate under the same general principles.
- b. The sample is placed in an environment, the temperature of which is regulated by a temperature programmer. Changes in the sample are monitored by an appropriate device which produces an electrical output which is the analogue of the chemical or physical change occurring to the sample. The output is amplified electronically and fed to an output device such as a computer or recorder.
- c. The temperature programmer is capable of either holding the temperature of the sample environment constant (isothermal operation) or varying the temperature as a linear function of time, the rate of which is selectable (dynamic operation).

ANNEX A to  
STANAG 4515  
(Edition 1)

- d. The output device plots directly the change of the property measured against temperature in dynamic mode or against time in isothermal mode, so that the change in the property under study becomes immediately obvious.

### 3. DEFINITION OF TERMS

- a. A number of terms are used to describe the various points of interest on the resultant plots when change of property is measured against temperature or time. The more commonly used terms are defined below and illustrated in figure A-1.
- b.  $T_g$  the glass transition temperature, is measured at its mid-point. This is defined as the point at which the bisector of the angle made between the extrapolated baseline recorded before the transition and the extrapolated baseline recorded after the transition, intersects the DSC curve. It is the temperature at which a polymeric explosive changes from a flexible rubbery state to a rigid glassy condition.
- c.  $T_i$  initial temperature, is the temperature at which the first deflection from the base line is observed for a chemical reaction.
- d.  $T_p$  peak maximum temperature, is the temperature at which the peak maxima or minima is observed.
- e.  $T_f$  final temperature, is the temperature, after a peak, at which no further deflection from the base line is observed.
- f.  $T_m$  onset temperature of melting, is measured as the point of intersection of two tangents, one drawn to the curve before commencement of the event, the other to a point on the steepest part of the transition. The same principle may be applied to a phase transition.
- g.  $T_e$  extrapolated onset temperature. It is measured as the point of intersection of two tangents, one drawn to the curve before commencement of the event, the other to a point on the steepest part of the transition.
- h.  $\Delta H_f$  heat of fusion, is the quantity of heat absorbed in the transformation of solid to liquid. This is determined by measurement of the area beneath the melting transition. A fuller definition can be found in ASTM E 793.85 (Standard Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry) (US publication).

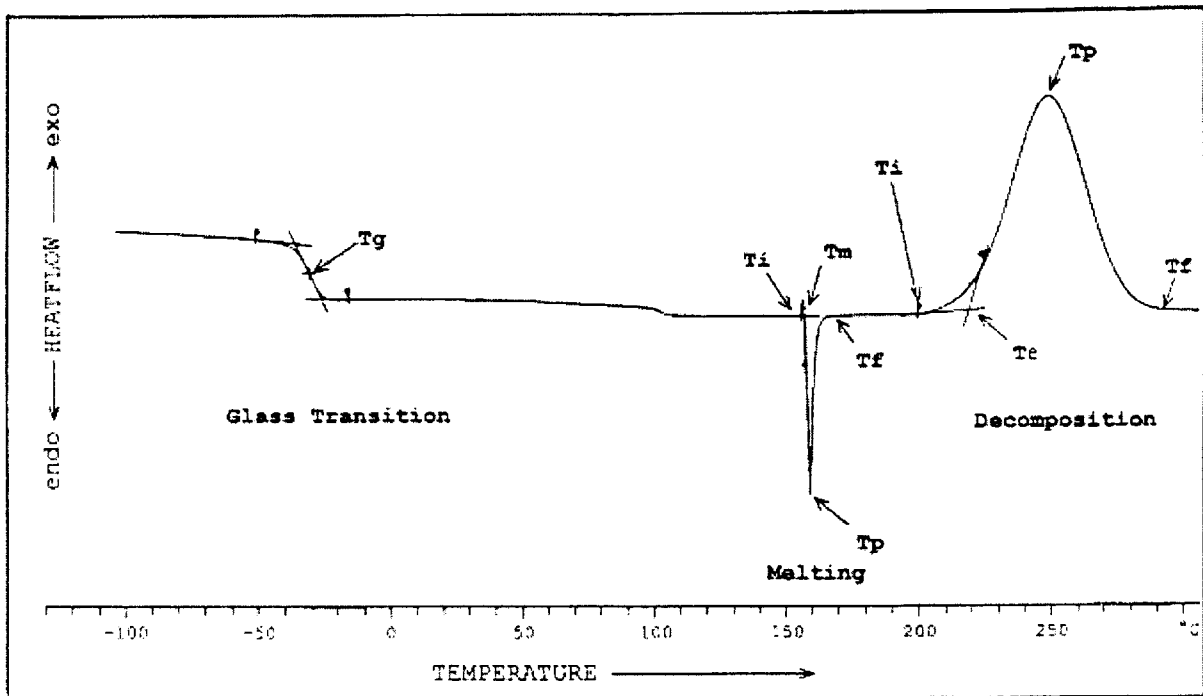


Figure A-1

#### 4. PRINCIPLE OF OPERATION

##### a. Differential Thermal Analysis, DTA

- (1) DTA records the difference in temperature between a substance and a thermally inert reference material, when both are subjected to the same thermal conditions. Sample and reference holders are each fitted with their own temperature sensing device, usually thermocouples connected in opposition. Sample and reference holders are fitted to a heat sink (usually a metal block or wafer) which is surrounded by a single heat source (furnace) which can be programmed to raise the temperature of both sample and reference at a predetermined rate. A generalised DTA system is shown in figure E-1.
- (2) If there are no transitions or reactions occurring within the sample, the difference in temperature between sample and reference ( $\Delta T$ ) is effectively zero. Temperature differences between the sample and reference are brought about by either endothermic or exothermic transitions or reactions within the sample pan. During endothermic transitions the sample undergoes "isothermal arrests", whereby its temperature remains relatively constant during the transition although there is an input of heat into the sample during this transition. The reference temperature continues to rise at the predetermined rate over this period hence a differential temperature exists between sample and reference, the sample lagging the reference. Conversely, during exothermic reactions, the heat evolved from the sample gives rise to a temperature difference between the sample and reference where the  $\Delta T$  signal has the opposite polarity. These changes lead to a departure from the  $\Delta T=0$  baseline during transitions, resulting in a peak in the output signal. When the transition is over, the sample "catches up" with the reference and the signal returns to the steady state as was observed before the transition. A gradual return to the baseline is observed due to the relatively low thermal conductivity of the sample crucible material.

ANNEX A to  
STANAG 4515  
(Edition 1)

- (3) When the technique is used in conjunction with a photodetector system, strategically placed above the sample, the ignition temperature can be assessed. A schematic representation is shown in figure E-2

b. Differential Scanning Calorimetry, DSC.

- (1) This technique measures the heat flow to/from a sample as it undergoes transitions in a thermally controlled environment. Two types of instrumentation can be used for measuring heat flow by differential scanning calorimetry - Power Compensation DSC and Heat flow DSC.
- (2) A Power Compensation DSC consists of individual sample and reference holders each fitted with its own heater and platinum resistance thermometer. In normal operation, the sample pan contains the explosive and the reference pan can be left empty or contain some inert material such as alumina. The system is operated by two electronic control loops. One is for the average temperature control, so that the temperature of sample and reference can be increased at a predetermined rate. The second loop ensures that if a temperature difference develops between reference and sample (due to exothermic or endothermic reaction in the sample) the power input is adjusted to remove this difference. Thus the temperature of sample and reference is kept the same by the continuous and automatic adjustment of the heater power of either the sample or the reference element depending on whether the sample undergoes exothermic or endothermic changes. Hence a signal is produced which is directly proportional to the difference between the heat input to the sample and that to the reference. The area beneath the curve is a direct measure of the heat involved in bringing about the transition i.e. heat flow to/from the sample ( $dH/dt$ ) which is usually measured in milliwatts.
- (3) A schematic diagram of a power compensation DSC is shown in figure E-3(b).
- (4) Heat flow DSC (heat flux DSC) instruments operate on the DTA principle which can be represented as shown in figure E-3(a). Mathematical manipulation of the measured DTA signal is necessary to obtain values of heat flow to/from the sample to bring about the transition. The thermal analogue of Ohm's Law is used,

$$dH/dt = \Delta T/R_{th}$$

where  $dH/dt$  is the heat flow

$\Delta T$  is the differential temperature (K)

$R_{th}$  is the thermal resistance to heat flow between sample pan and holder ( $K.s.J^{-1}$ ).

The heat flow to/from the sample is given by the difference in heat flows to the reference and sample holders.

$$dH/dt = dQ_s/dt - dQ_R/dt$$

where  $dQ_s$  = heat flow to sample

$dQ_R$  = heat flow to reference

Applying the "thermal" Ohm's Law:

$$dH/dt = (T_C - T_S)/R_{th} - (T_C - T_R)/R_{th}$$

where  $T_C$  is the temperature of the heat sink  
 $T_S$  and  $T_R$  are the temperatures of the sample and reference  
 respectively

Thus,  $dH/dt = -(T_S - T_R)/R_{th}$

The temperature difference given by the output from the two thermocouples  
 connected in opposition is given by:

$$(T_R - T_S) = \Delta T$$

and  $\Delta T = U/S$

where  $\Delta U$  is the thermocouple potential ( $\mu V$ )  
 $S$  is the thermocouple sensitivity ( $\mu V K^{-1}$ )

It follows that,

$$dH/dt = \Delta U/R_{th}S$$

$dH/dt$  has a negative value for exothermic reactions and a positive value for  
 endothermic reactions.

- (5) Both  $R_{th}$  and  $S$  are functions of temperature and can be combined as the  
 calorimetric sensitivity. This is determined by calibration using the known heat  
 of fusion of a standard reference material, such as biphenyl, indium, tin, or  
 other pure metals, depending on the temperature of interest. The heat of fusion  
 gives a measure of the measuring cell sensitivity in  $\mu V mW^{-1}$ . This term is also  
 referred to as cell constant.

c. Thermogravimetric Analysis (TGA)

- (1) TGA measures changes in weight of a sample as a function of  
 temperature/time. Measurements can be carried out with a gas flow of air,  
 nitrogen or another specified gas. The technique is useful in distinguishing  
 phase changes from weight changes caused by chemical reactions. The  
 technique becomes even more useful if connected directly to a Fourier  
 Transform Infrared Spectrometer for evolved gas analysis (EGA) or to a mass  
 spectrometer (MS). Gaseous decomposition products and volatile species can  
 readily be identified making the task of characterising transitions in unknown  
 compositions much simpler. Samples are weighed directly onto a sample pan  
 assembly fitted to the TGA or with a microbalance. The sample pan assembly  
 is completely surrounded by a furnace for control of the sample temperature. It  
 is possible to purge the furnace volume with inert or reactive atmospheres.
- (2) TGA is normally carried out using one of the schematic representations shown  
 in figure E-4.

ANNEX A to  
STANAG 4515  
(Edition 1)

d. General Summary

- (1) The processes detectable using the three principal thermal analysis techniques are summarised in table A-1.

Process	DTA	DSC	TGA
Phase transformation	+	+	-
Melting transitions	+	+	-
Purity	-	+	-
Sublimation	+	+	+
Glass transition	-	+	-
Heat capacity	-	+	-
Desorption	+	+	+
Adsorption	+	+	+
Chemical reaction	+	+	+
Decomposition	+	+	+
Oxidation/reduction	+	+	+

Table A-1

NOTE: Processes such as sublimation may cause practical problems in that the sublimate will condense in the cooler parts of the instrument. Decontamination may be necessary at the end of each run performed and care must be exercised to prevent sublimates entering the internal workings of an instrument eg TGA balance or electronics. Efficient purging is, therefore, essential to minimise this possibility.

NOTE: Although thermal analysis techniques can be used to determine glass transition, they may not necessarily be the best technique available. Glass transition is a mechanical parameter and as such mechanical analysis techniques, for example Dynamic Mechanical Analysis (DMA) or Thermomechanical Analysis (TMA), may prove to be more suitable.

5. GENERAL CONSIDERATIONS IN PERFORMING THERMOANALYTICAL STUDIES OF EXPLOSIVE MATERIALS

- a. Safety of the operator is of primary importance and analyses will generally be carried out on the smallest sample size necessary.
- b. Heating rates shall be carefully chosen to ensure that the decomposition reactions are controlled and do not lead to thermal runaway or ignition of samples. The only exception to this is for the study of ignition reactions of primary explosives, black powders or pyrotechnics using DTA, when heating rates of up to 50°C/min have to be used. Serious damage to TGA and DSC instruments is likely to occur if reactions are not carried out under controlled conditions.
- c. Generally, most analyses shall be performed in an inert gas atmosphere. This is necessary for a number of reasons:
  - (i) To purge away evolved gases, protecting the cell from corrosive products.
  - (ii) Displacement of atmospheric oxygen to avoid unwanted oxidation.
  - (iii) To purge away evolved gases which may upset the equilibrium of certain chemical reactions.
  - (iv) As a carrier to FTIR in TGA/evolved gas analysis (EGA) or mass spectrometry (MS).

- d. Some materials eg pyrotechnics, rely on the presence of air for their preferred reaction to proceed. Careful consideration of sample reactions will have to be conducted before deciding on the gas environment to be used.
- e. The physical characteristics of the sample can also influence observations made. Pressed samples behave differently to loose powders and the degree of compaction of the sample can also affect the course of the reaction. Particle size will also affect the results as the rate of reaction may be highly dependant on the surface area. Hence sample preparation is of paramount importance and must be prescribed if the results are to be used for comparison purposes. Generally primary explosives are used without further treatment. The individual components of pyrotechnics may separate during storage. Careful mixing is advisable prior to removal of the sample for analysis. Generally the sample can then be used without further treatment.
- f. Processes involving the weighing of samples and the handling of sample crucibles should be conducted using non-sparking tools and implements (eg spatulas). These should be made of either phosphor-bronze or ceramic.
- g. It is preferable that thermograms are started at room temperature. However there may be occasions when it is necessary to start the thermogram at lower temperatures; for example when measuring the glass transition of nitroglycerin. Never place explosive materials into a hot furnace. Never attempt to remove samples from the thermal equipment until ambient temperature has been restored. Cooling accessories may be used to facilitate cooling of the sample environment/furnace.
- h. Recommended heating rates and sample sizes for the different types of explosive materials are given in tables A-2 and A-3:

EXPLOSIVE MATERIAL	TEST TECHNIQUE			COMMENTS
	DTA	DSC	TGA	
Secondary detonating explosives	+	+	+	5mg maximum weight. 10°C min <sup>-1</sup> maximum heating rate.
PBX	+	+	+	
Propellants	+	+	+	
Pyrotechnics	+	+	+	The following conditions are recommended. sample size <10mg and heating rate 10°C min <sup>-1</sup> maximum. or sample size <20mg and heating rate 5°C min <sup>-1</sup> .
Black Powder	+	+	+	

Table A-2.

ANNEX A to  
STANAG 4515  
(Edition 1)

PRIMARY EXPLOSIVE	TEST TECHNIQUE	TEST CONDITIONS	COMMENTS
Unknown mixture	DTA DSC	Sample size <1mg. Heating rate 10°C min <sup>-1</sup> .	DTA is the most robust of these techniques.
Well characterised primary explosives	DTA DSC TGA	Sample size 2mg max. Heating rate 5°C min <sup>-1</sup> .	These conditions should only be used by experienced operators.
Less well characterised primary explosives	DSC TGA	Sample size 2mg max. Heating rate between 1 - 10°C min <sup>-1</sup> .	When using the DSC technique, to prevent over pressurisation of the pans they should not be sealed or the lid should be pierced.

Table A-3.

**NOTE:** The maximum sample size and heating rates quoted in tables A-2 and A-3 are based on experimentation, but with due consideration to both safety to the operator and damage to the equipment. It has been found that the sample sizes quoted were able to provide measurable, homogenous and representative samples that were small enough to ensure safety to the operator and to the equipment.

- i. By carrying out thermal investigations within the recommended limits, the possibility of explosion, thermal runaway and risk of damage to equipment will be minimised but never totally excluded. As a general rule the possibility of explosion will diminish with smaller sample sizes and lower heating rates.
- j. It is also essential to use a portable extraction system in close proximity to the instruments used to remove any harmful evolved gases resulting from decomposition reactions.

**TEST PROCEDURES****1. PROCEDURE 1. DIFFERENTIAL THERMAL ANALYSIS****a. Apparatus for all DTA applications**

- (1) A Differential Thermal Analyzer capable of heating rates up to  $50^{\circ}\text{C min}^{-1}$  and automatically recording the differential temperature between sample and reference materials with the required sensitivity and precision. It should have an upper temperature capability of about  $1000^{\circ}\text{C}$ .
- (2) Sample crucibles manufactured from material which is inert to the material under test. They should be large enough to be able to accommodate up to 30mg of sample and be robust enough to withstand the mechanical forces and high temperatures encountered during ignition reactions. In special investigations (eg autocatalysis) a loosely fitting lid or a pierced lid can be used. Ceramic materials or platinum are considered suitable. Ceramic is the preferred material since the crucibles are readily cleaned in a muffle furnace or by boiling in concentrated acids.
- (3) Purge gas supply and associated flow controller.
- (4) Inert reference material which is not thermally active over the temperature range to be used. For most applications, alumina has been found to be suitable.
- (5) Balance capable of measuring to 0.1mg.

**b. Additional apparatus for temperature of ignition studies.**

- (1) 1kg dead-weight press with a drift of slightly smaller diameter than the internal diameter of the sample crucibles.
- (2) Photodetector and associated signal amplification circuitry.
- (3) Adaptor to fit the photodetector to the top of the furnace.

**NOTE:** Further details of the apparatus used for ignition studies can be found in:

- (4) DQA/TS Materials Technical Note 246. Temperature of Ignition/Differential Thermal Analyzer. C J Hutchinson, 1985.

**c. Calibration**

- (1) Since a DTA instrument is used only semi-quantitatively for measurement of endothermic and exothermic transitions, accurate calibration of the heat of transition reaction is not generally necessary.
- (2) Calibration should be performed to the level recommended by the instrument manufacturer but shall not exceed  $\pm 2^{\circ}\text{C}$ . Generally, temperature calibration will be performed at at least two points using standard reference materials with melting point onset close to the limits of the temperature range of interest.
- (3) Calibration will be carried out using the same type of sample crucible, heating rate, purge gas and purge gas flow rates as will be used for test measurements.

ANNEX B to  
STANAG 4515  
(Edition 1)

- (4) Typical standard reference materials used for temperature and enthalpy calibration are shown in table B-1:

Material	Melting Point [°C]	Enthalpy [J g <sup>-1</sup> ]
Biphenyl	69.3	120.41
Indium	156.6	28.46
Zinc	419.5	111.18
Aluminium	660.2	397.0
Silver	960.8	102.81

Table B-1.

d. Sample preparation.

- (1) Samples shall be representative of the material being studied and should be prepared to achieve good thermal contact between the sample and container.
- (2) When studying temperatures of ignition of pyrotechnics/black powder, the requisite amount of sample is added to the crucible and is then pressed for 30 seconds using the 1kg dead-weight press.

e. Procedure

- (1) Weigh accurately the recommended quantity of a representative portion of the sample into a tared crucible and record the sample weight.
- (2) Load the sample and reference crucibles into the instrument.
- (3) Purge the sample chamber with an appropriate gas and record the flow rate.

NOTE: Temperatures of ignition are generally performed in static air with no purge gas.

- (4) Fit the photodetector system to the furnace if temperatures of ignition are being studied.
- (5) Heat the sample at the recommended heating rate over the temperature range of interest and record the thermogram produced.
- (6) For temperature of ignition studies, also record the photodetector output as a function of furnace temperature.
- (7) Repeat using a further representative portion of the sample after allowing the furnace to cool to room temperature.

f. Analysis

- (1) Figure F-1 of annex F shows a typical DTA thermogram and indicates some typical data points that can be determined.
- (2) Figure F-2 of annex F shows a typical photodetector output as a function of furnace temperature and indicates the data points that can be determined.

g. Reporting

Examine the thermograms and report initial temperature and peak maxima of any endothermic or exothermic events. Wherever possible identify the thermal effect. For temperature of ignition studies, determine the temperature of ignition as the onset of the rapid increase in light output detected on the production of a light "flash" upon sample ignition.

2. PROCEDURE 2. DIFFERENTIAL SCANNING CALORIMETRYa. Apparatus

- (1) Differential Scanning Calorimeter capable of heating rates up to  $20^{\circ}\text{C min}^{-1}$  and automatically recording the differential heat flow between the sample and reference materials with the required sensitivity and precision. It should have an upper temperature capability of at least  $600^{\circ}\text{C}$ .
- (2) Sample crucibles manufactured from material which is inert to the material under test and of high thermal conductivity. Typical materials include aluminium, gold and platinum. Aluminium is the most commonly used material because of its lower cost.
- (3) Purge gas supply and associated flow controller.
- (4) Generally, it is not necessary to use a reference material in the reference crucible. However where a reference is considered necessary an inert reference material which is not thermally active over the temperature range should be used. For most applications, alumina has been found to be suitable.
- (5) Balance capable of measuring to 0.01mg.
- (6) Crucible sealing press.

b. Calibration

- (1) Calibration is performed by measurements of the heats of fusion and melting points of standard reference materials. The instrument is calibrated using the same type of sample crucible, heating rate, purge gas and purge gas flow rates as will be used for the test measurements.
- (2) Typical standard reference materials used for temperature and enthalpy calibrations are shown in table B-2:

ANNEX B to  
STANAG 4515  
(Edition 1)

Material	Melting point [°C]	Enthalpy [J g <sup>-1</sup> ]
Biphenyl	69.3	120.41
Indium	156.6	28.46
Lead	327.5	23.1
Zinc	419.5	111.18

Table B-2.

- (3) Calibration should be performed to the level recommended by the instrument manufacturer but shall not exceed a deviation in melting point onset of  $\pm 0.5^{\circ}\text{C}$  and heats of fusion of  $\pm 2\%$ .

c. Sample preparation

Samples shall be representative of the material being studied and should be prepared to achieve good thermal contact between the sample and container.

d. Procedure

- (1) Weigh accurately the recommended quantity of a representative portion of the sample into a tared container with lid.
- (2) Seal the lid onto the crucible using the sealing press. Reweigh the container plus any cut residue and record the sample weight.

NOTE: For some applications eg substances sensitive to oxidation, it may be necessary to hermetically seal the crucible under an inert gas atmosphere.

For most applications standard crucibles and lids will be used. These generally cannot withstand internal pressures of  $>2$  atmospheres and effectively allow the venting of evolved gases without the risk of explosion.

Alternatively the lid can be pierced with a pin. This can prevent distortion and resultant poor contact with the sensor.

- (3) Load the sample and reference material crucibles into the instrument.
- (4) Purge the sample chamber with the inert gas at the flow rate recommended by the manufacturer and record the gas flow rate.
- (5) Heat the sample at a rate complying with tables A-2 and A-3 over the temperature range of interest and record the thermogram produced.

NOTE: The upper temperature limit is governed by the instrument being used and also the crucible material. Some instruments have an upper temperature limit of  $600^{\circ}\text{C}$  but most can be used to  $725^{\circ}\text{C}$ . However, with these instruments, an upper temperature limit of  $640^{\circ}\text{C}$  is recommended if using aluminium crucibles as aluminium melts at  $660.2^{\circ}\text{C}$ .

- (6) Repeat, using a further representative portion of the sample, when the furnace has returned to room temperature.

e. Analysis

Figure F-3 of annex F shows a typical DSC thermogram and indicates some typical data points that can be determined.

f. Reporting

- (1) Examine the thermograms and report initial temperatures and peak maxima of any endothermic or exothermic events. Wherever possible, identify the thermal effect.
- (2) When reporting and interpreting data consideration should be given to the following points:
  - (a) Under the test conditions quoted it is doubtful whether the heat of fusion of some explosive materials can be measured using DSC. For example, RDX decomposes upon melting and, therefore, endothermic fusion and exothermic decomposition occur simultaneously and the magnitudes of both peaks are obviously affected.

NOTE: Some test centres have noted that heat of fusion for RDX can be separated from decomposition by using a higher heating rate.

- (b) Care should also be exercised with the initial melting peak observed at about 78°C in RDX/TNT mixtures. This peak is due to the melting of the RDX/TNT eutectic consisting of 2% RDX/98% TNT and not the melting transition of TNT. The remaining 2% TNT melts at about 80°C and is not observed since it is contained within the melting range of the eutectic. For most RDX/TNT compositions, all of the TNT present melts as part of the eutectic.

3. PROCEDURE 3. THERMOGRAVIMETRIC ANALYSISa. Apparatus.

- (1) Thermogravimetric analyzer capable of heating rates up to 20°C min<sup>-1</sup>, weighing to 0.01mg and automatically recording weight loss/gain as a function of temperature. It should have an upper temperature capability of about 1000°C.
- (2) Sample crucibles manufactured from material which is inert to the material under test. Typical materials include ceramic, platinum and aluminium. Ceramic is the preferred material since the crucibles are readily cleaned in a muffle furnace or by boiling in concentrated acids.
- (3) Purge gas supply and associated flow rate controller.

b. Calibration

- (1) The balance should be calibrated using a 20, 50 or 100 mg weight, accurate to 0.005%. Class E2 weights are considered suitable.

ANNEX B to  
STANAG 4515  
(Edition 1)

- (2) Temperature calibration is achieved by measurement of the melting points of standard reference materials in the form of fusible links, by measurement of the Curie point temperatures of standard materials (i.e. loss of ferromagnetic properties) or by any other suitable method.

**NOTE:** Fusible links are short lengths of pure metal wire connected to the balance pan and carrying a small weight. When the metal melts a weight change is experienced by the balance.

Curie elements change their ferromagnetic properties at a certain temperature. This is converted into a TGA signal using an external permanent magnet.

- (3) Typical standard reference materials used for melting point temperature calibrations are shown in table B-3:

Material	Melting point (°C)
Indium	156.6
Tin	232.0
Zinc	419.5
Aluminium	660.2

Table B-3.

- (4) Typical standard reference materials used for Curie point temperature calibration are shown in table B-4:

Material	Curie point (°C)
Nickel	357.0
Trafoperm <sup>1</sup>	745.6

Table B-4.

- (5) Calibration should be performed to the level recommended by the instrument manufacturer but shall not exceed a deviation in transition temperatures of  $\pm 5^{\circ}\text{C}$ .

c. Sample preparation

Samples shall be representative of the material being studied.

d. Procedure

- (1) Purge the sample chamber with inert gas and record the gas flow rate.
- (2) Tare the balance mechanism.
- (3) Introduce the sample into the sample crucible.

<sup>1</sup> Trafoperm is available from Mettler Toledo as a ready prepared calibration material

- (4) Record the sample weight.
- (5) Heat the sample at the recommended heating rate over the temperature range of interest. Record any weight changes experienced by the sample as a function of temperature.
- (6) Allow the furnace to cool and repeat the complete procedure again, using a further representative portion of sample.

e. Analysis

Figure F-4 of annex F shows a typical TGA thermogram and indicates some typical data points that can be determined.

f. Reporting

- (1) Weight losses/gains between the start and end of reaction should be calculated as a percentage. Weight loss steps between plateau regions should be measured as percentages and, wherever possible, weight loss steps should be assigned to thermal effects eg loss of volatile matter, decomposition etc. .
- (2) The derivative weight loss trace should also be recorded and presented. This is a measure of the rate of weight loss as a function of time/temperature and is characteristic for a material or composition. It generally consists of a series of peaks, each corresponding to a weight loss/gain step. It can be used as a thermogravimetric "fingerprint" for characterisation purposes. Record the peak temperatures of the derivative TGA trace.



1. **FURTHER APPLICATIONS**

- a. Purity programs applied to DSC melting transitions of components can give useful information on the identity and purity of major components provided impurities are dissolved in the liquid phase of the component under study.
- b. Heats of fusion can be used to estimate the quantitative composition of known mixtures. Only DSC can be used to study heats of fusion.
- c. Under suitable conditions DSC can provide a quick and convenient procedure for the determination of specific heat capacity.
- d. Kinetic analysis can be applied to decomposition reactions and kinetic parameters calculated. This information may be useful in assessing the stability of explosives at various temperatures. Kinetic analysis can not be undertaken using DTA as this technique is not quantitative enough for such investigations.



<b>NATO STANAG 4515 DATA SHEET (Side A)</b>	
<b>Report Reference Number:</b> (Unique Reference Number)	<b>Page</b> <u>    </u> <b>of</b> <u>    </u> <b>Page(s)</b>
<p style="text-align: center;"><b>TEST SITE INFORMATION</b></p> <p>Laboratory: (Name of Laboratory)</p> <p>Date: (Date that form was completed)</p> <p>Test Procedure: (Name of test procedure used)</p> <p>Date Tested: (Date of test period)</p> <p>POC: (Point of contact)</p>	<p style="text-align: center;"><b>TEST CONDITIONS</b></p> <p>Instrument Model:</p> <p>Temperature Range:</p> <p>Heating Rate:</p> <p>Data Acquisition Rate (Sec/pt):</p> <p>Purge Gas:</p> <p>Purge Gas Flow Rate:</p>
<p style="text-align: center;"><b>SPECIMEN INFORMATION</b></p> <p>Sample designation:</p> <p>Sample source/Manufacturer:</p> <p>Lot or ID No:</p> <p>Date of Manufacture or Receipt:</p> <p>Form of material:</p> <p>Sample weight:</p> <p>Particle size</p>	<p style="text-align: center;"><b>SAMPLE PREPARATION</b></p> <p>Sample preconditioning and preparation details:</p> <hr/> <p style="text-align: center;"><b>COMPOSITION</b></p> <p>Component and percentage details:</p> <hr/> <p style="text-align: center;"><b>DATA SENT TO</b></p>

ANNEX D to  
STANAG 4515  
(Edition 1)

NATO STANAG 4515 DATA SHEET (Side B)	
Report Reference Number: (Unique Reference Number)	Page ___ of ___ Page(s)
<b>RESULT SUMMARY</b>	
<b>TEMPERATURE (°C)</b>	<div style="text-align: center;"><b>OBSERVATIONS</b></div> <div style="text-align: center; margin-top: 10px;"><u>Phase Transition Reaction</u></div> <div style="margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div> <p>Key   <math>T_g</math> = Glass Transition Temp.</p> <p>         <math>T_i</math> = Initial Temp.</p> <p>         <math>T_m</math> = Melting Temp.</p> <p>         <math>\Delta H_f</math> = Heat of Fusion</p> </div> <div> <p><math>T_p</math> = Peak Max Temp.</p> <p><math>T_e</math> = Extrapolated Onset Temp. (decomp.)</p> <p><math>T_f</math> = Final Temp.</p> </div> </div> </div>
<b>THERMOGRAM</b>	
<b>COMMENTS</b>	

## NATO STANAG 4515 DATA SHEET (Side A)

Report Reference Number: **EXAMPLE**  
(Unique Reference Number)

Page 1 of 2 Page(s)

**TEST SITE INFORMATION**

Laboratory: DRA Chorley  
(Name of Laboratory)

Date: 19th March 96  
(Date that form was completed)

Test Procedure: DSC  
(Name of test procedure used)

Date Tested: 18th Sept 95  
(Date of test period)

POC:  
(Point of contact)

**TEST CONDITIONS**

Instrument Model: TA Instruments 910 DSC

Temperature Range: 50 - 300°C

Heating Rate: 10°C min<sup>-1</sup>

Data Acquisition Rate (Sec/pt): 0.6

Purge Gas: Nitrogen

Purge Gas Flow Rate: 80 cm<sup>3</sup> min<sup>-1</sup>

**SPECIMEN INFORMATION**

Sample designation: EDC1

Sample source/Manufacturer:

Lot or ID No:

Date of Manufacture or Receipt:

Form of material:

Sample weight: 1.7820 mg

Particle size

**SAMPLE PREPARATION**

Sample preconditioning and preparation details:

None

**COMPOSITION**

Component and percentage details:

HMX	70%
TNT	25%
RDX	4%
Beeswax	1%

**DATA SENT TO**

ANNEX D to  
STANAG 4515  
(Edition 1)

## NATO STANAG 4515 DATA SHEET (Side B)

Report Reference Number: **EXAMPLE**  
(Unique Reference Number)

Page 2 of 2 Page(s)

## RESULT SUMMARY

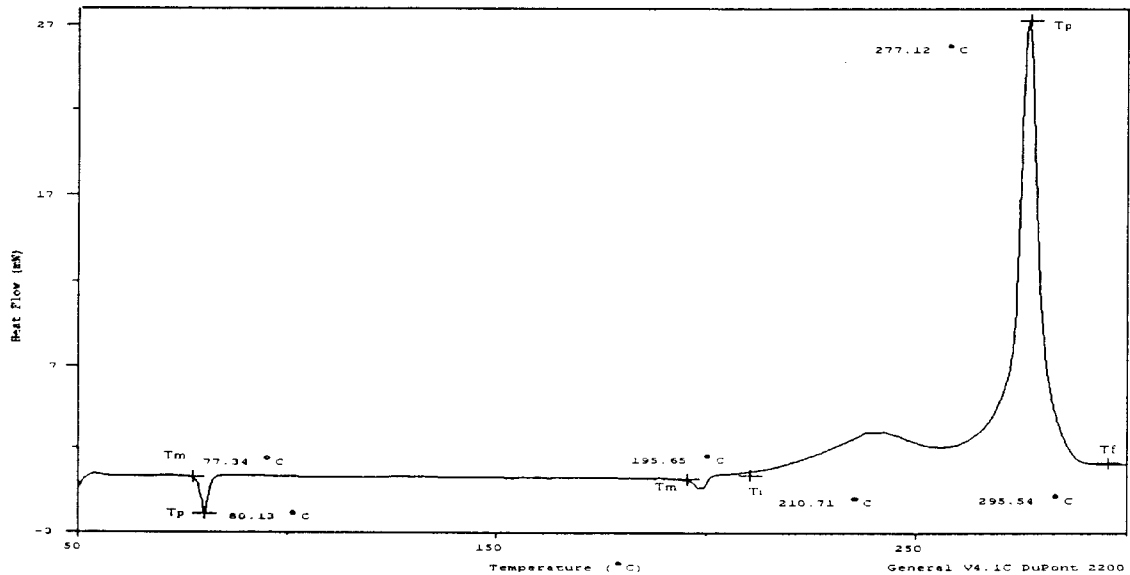
TEMPERATURE (°C)	OBSERVATIONS
	<u>Phase Transition Reaction</u>
	Key $T_g$ = Glass Transition Temp. $T_p$ = Peak Max Temp. $T_i$ = Initial Temp. $T_e$ = Extrapolated Onset Temp. (decomp.) $T_m$ = Melting Temp. $T_f$ = Final Temp. $\Delta H_f$ = Heat of Fusion
77.3 80.1 195.6 210.7 277.1 295.5	Onset of melting RDX/TNT eutectic. ( $T_m$ ) RDX/TNT eutectic melting transition peak max. ( $T_p$ ) Onset of melting of RDX. ( $T_m$ ) Decomposition exotherm onset. ( $T_i$ ) Decomposition exotherm max. ( $T_p$ ) Decomposition exotherm end. ( $T_f$ )

## THERMOGRAM

Sample: EDCL REFERENCE SAMPLE  
Size: 1.7820 mg  
Method: PBX  
Comment: N2 PURGE GAS 80 ML5/MIN

DSC

File: KMDSC.010  
Operator: KDM  
Run Date: 18-Sep-95 16:25



## COMMENTS

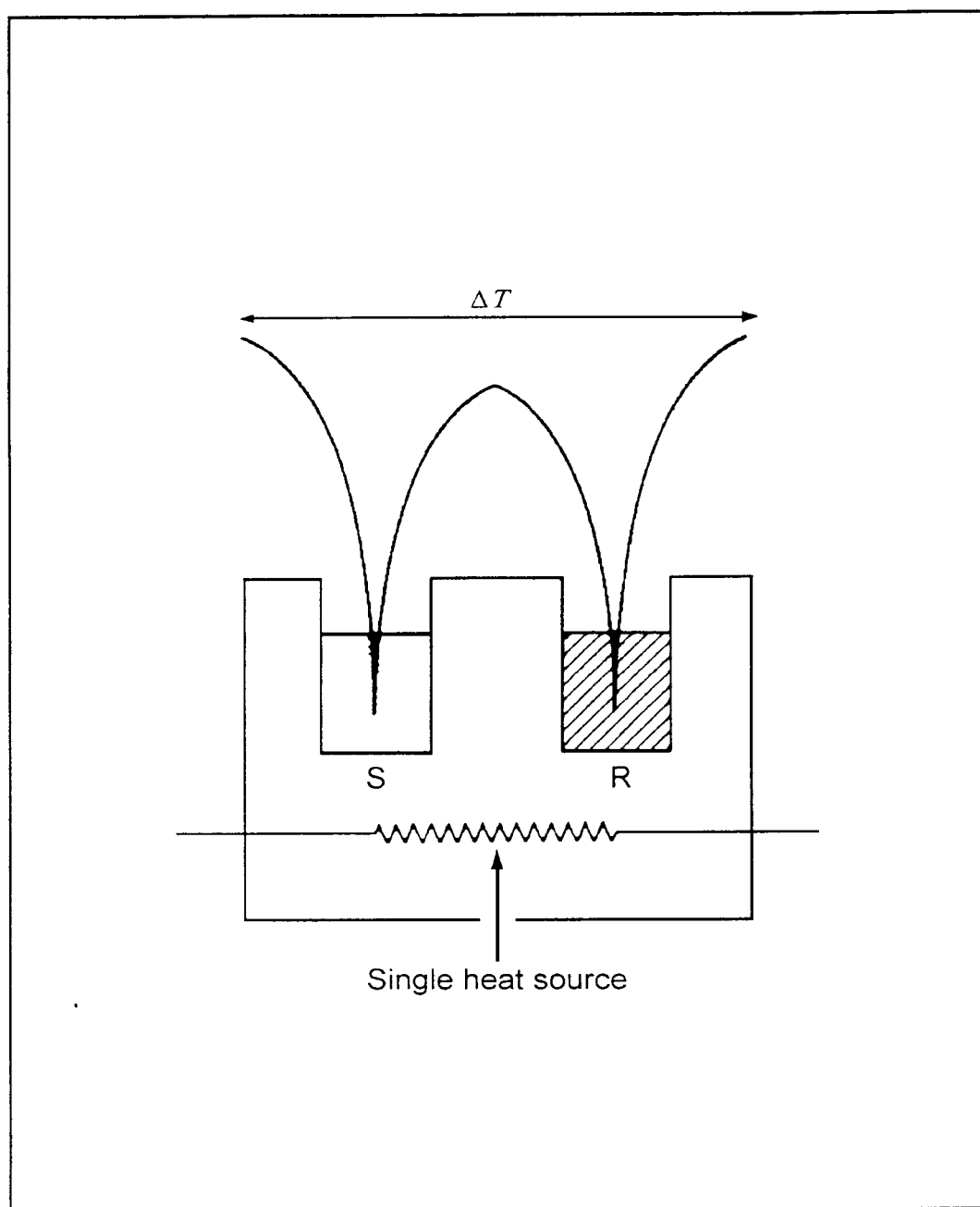


Figure E-1. DTA: Schematic Diagram

ANNEX E to  
STANAG 4515  
(Edition 1)

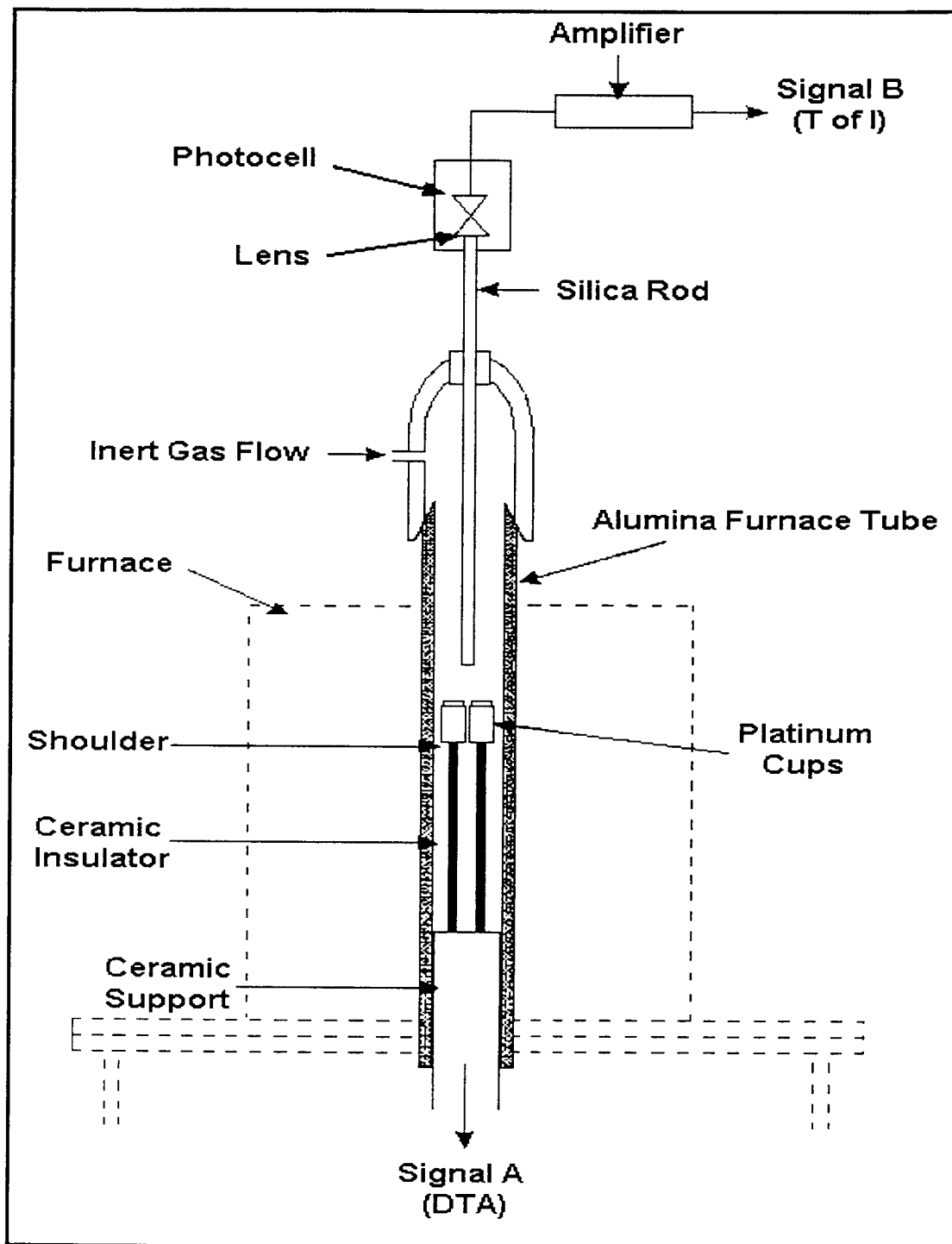


Figure E-2. DTAT of I: Schematic Diagram

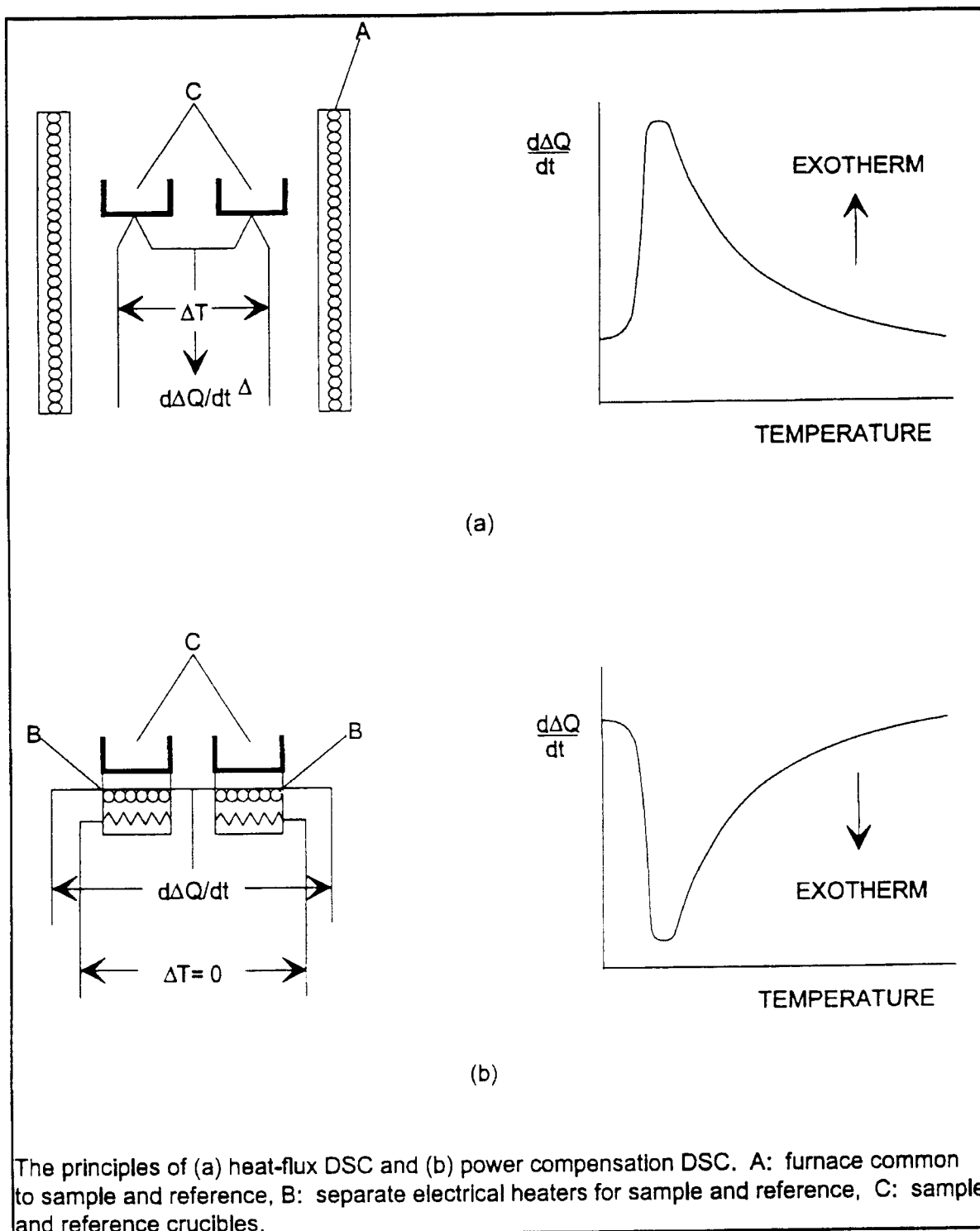


Figure E-3. DSC Operating Principles

ANNEX E to  
STANAG 4515  
(Edition 1)

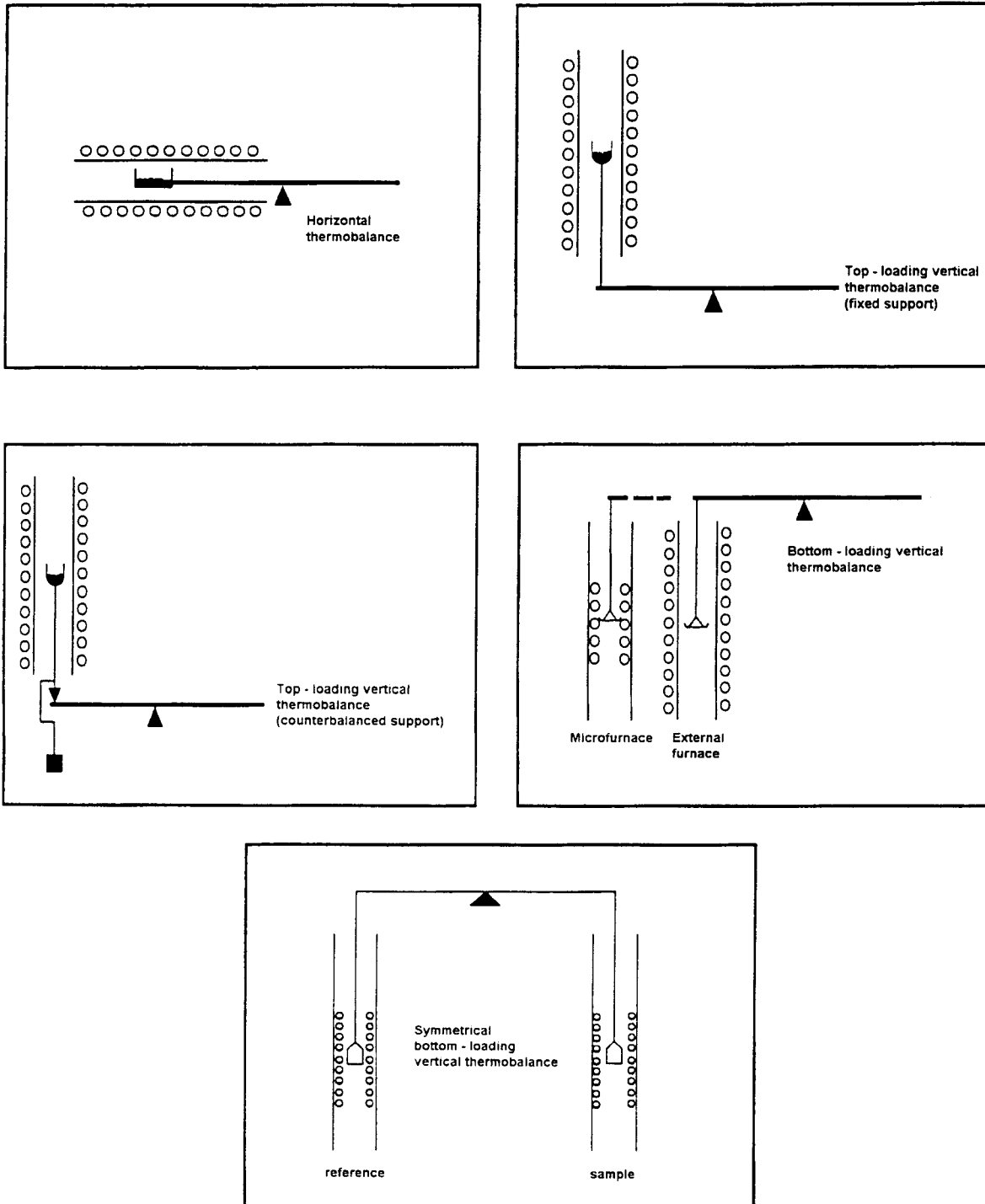


Figure E-4. TGA: Schematic Diagram

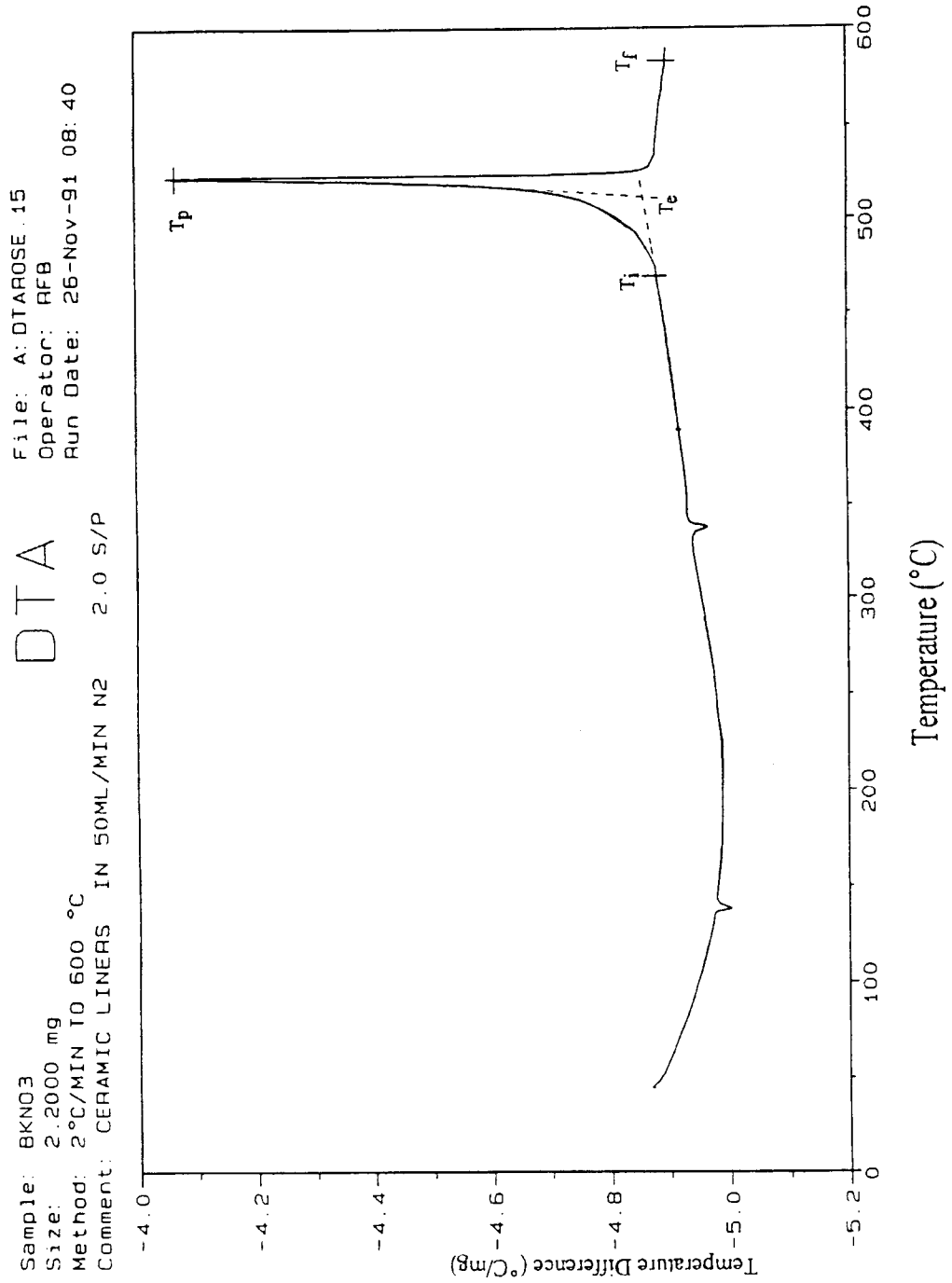


Figure F-1. Typical DTA Thermogram

ANNEX F to  
STANAG 4515  
(Edition 1)

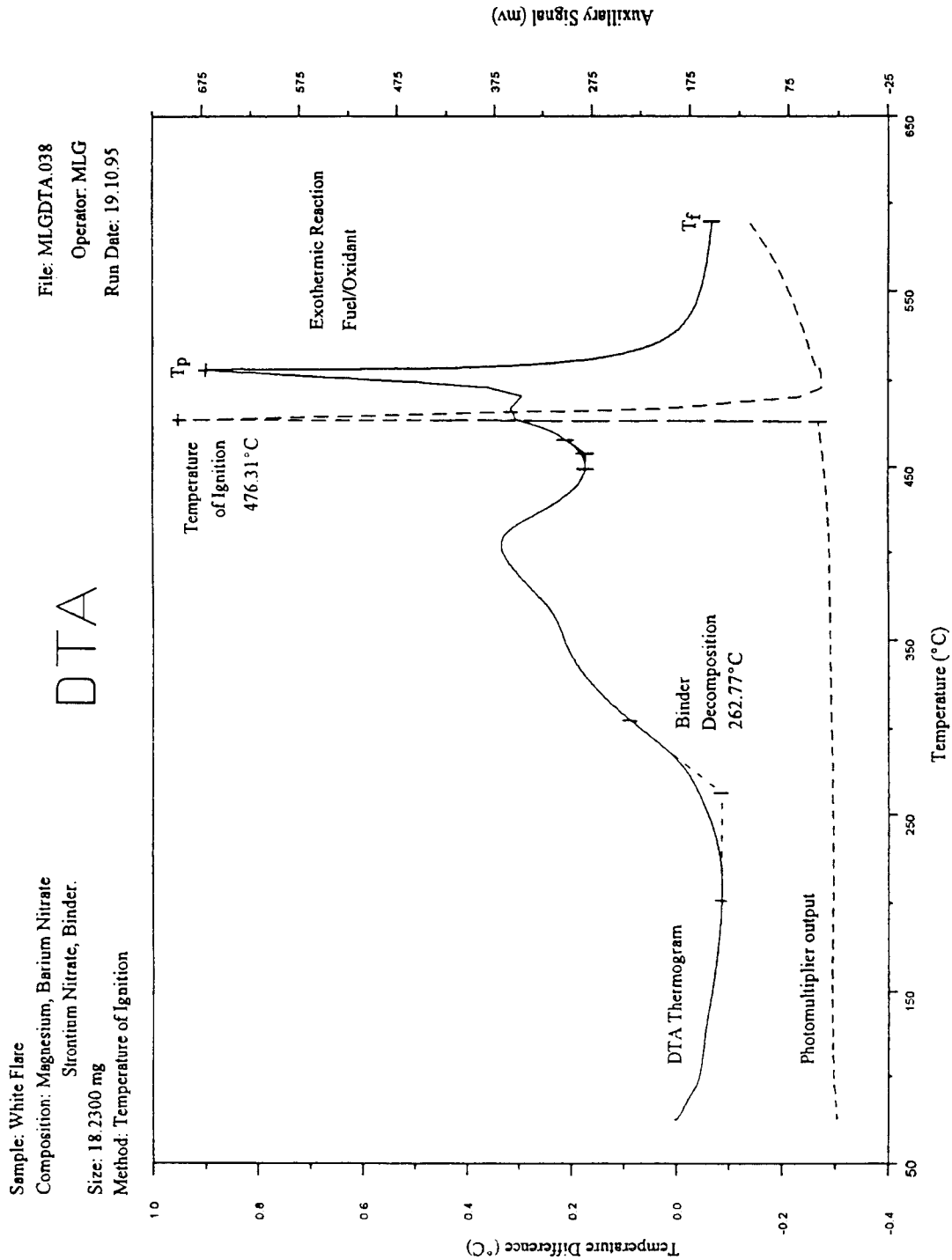


Figure F-2. Typical DTA / T of I Thermogram

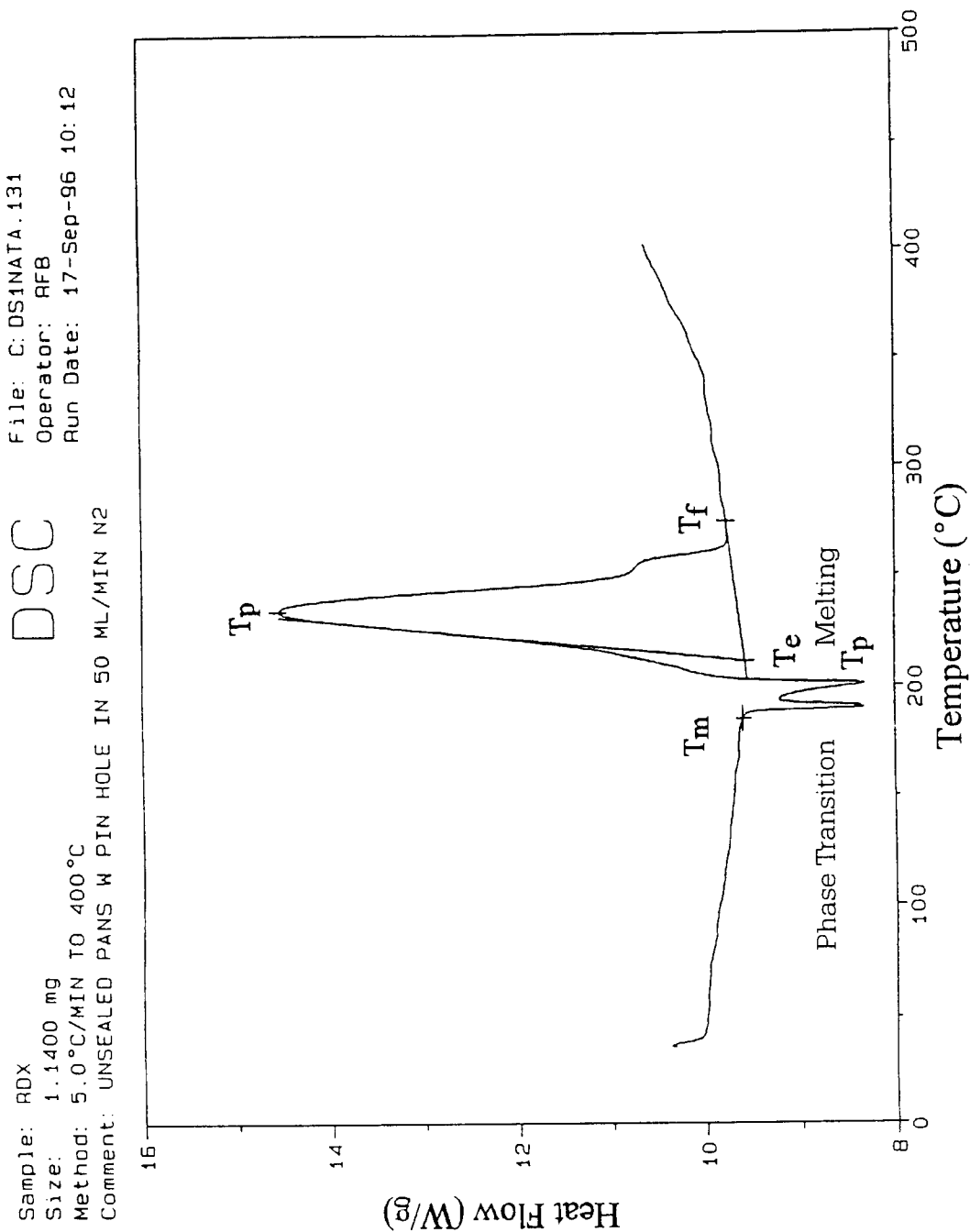


Figure F-3. Typical DSC Thermogram

ANNEX F to  
STANAG 4515  
(Edition 1)

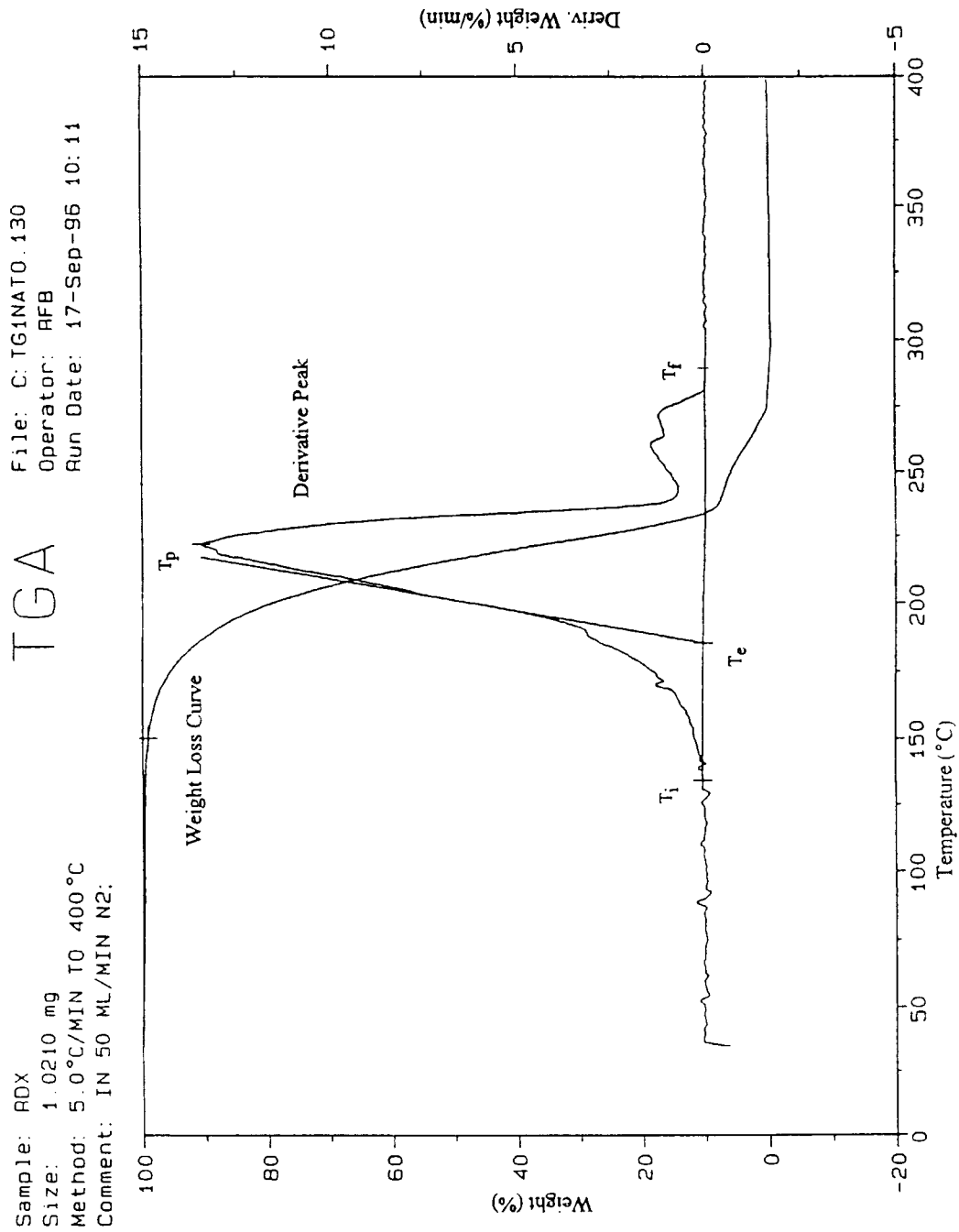


Figure F-4. Typical TGA Thermogram

RATIFICATION AND IMPLEMENTATION DETAILS  
STADE DE RATIFICATION ET DE MISE EN APPLICATION

EDITION: 1

N A T I O N	NATIONAL RATIFICATION REFERENCE DE LA RATIFICATION NATIONALE	NATIONAL IMPLEMENTING DOCUMENT NATIONAL DE MISE EN APPLICATION	IMPLEMENTATION / MISE EN APPLICATION					
			INTENDED DATE OF IMPLEMENTATION/ DATE PREVUE POUR MISE EN APPLICATION			DATE IMPLEMENTATION WAS ACHIEVED/ DATE REELLE DE MISE EN APPLICATION		
			NAVY MER	ARMY TERRE	AIR	NAVY MER	ARMY TERRE	AIR
BE	ZSP/OTAN 011557 of/du 13.11.01 Naval Staff / Etat-Major de la Marine	Not implementing/Ne met pas en application						
CA	2441-4515(A/DAPM 4-3) of/du 26.11.01	STANAG	01.02	01.02	01.02			
CZ	6/2-48/2001-1419 of/du 22.08.01	Czech Defence Standard No. 137601					09.01	09.01
DA	FKO MA/2 204.69-S4515 0200191-003 of/du 26.03.02	STANAG	07.02	07.02	07.02			
FR								
GE								
GR								
HU								
IT								
LU								
NL								
NO								
PL +	135/ROK/P of/du 11.05.02	STANAG						
PO								
SP								
TU *	TUDEL-02/STAN	STANAG		01.10				
UK	D/DStan/12/15/4515	STANAG						
US	OU5D(A&T) of/du 10.06.02	STANAG	06.02	06.02	06.02	06.02	06.02	06.02

\* See reservations overleaf/voir réserves au verso

+See comments overleaf/Voir commentaires au verso

X Service(s) implementing/Armées mettant en application

RESERVATIONS/RESERVES

TURKISH	The three test procedures described in this STANAG can only be applied on TNT explosives in Turkey.
TURQUIE	<i>Les trois procédures d'essai décrites dans ce STANAG ne peuvent s'appliquer qu'aux explosifs au TNT en Turquie.</i>

COMMENTS/COMMENTAIRES

POLAND	Resolutions of this agreement shall not be implemented in regulations and instructions that are directly addressed to the forces. Resolutions of this agreement shall be used by Military and Testing Institutes.
POLOGNE	<i>Les dispositions de cet accord ne seront pas transposées dans les règlements et instructions qui concernent directement les forces. Ces dispositions seront utilisées par les instituts militaires et d'essai</i>